

PCT/1B/04/51458
H

PCT/1B04/001120

IB04/51458
Certificate

Sertifikaat

REPUBLIEK VAN SUID AFRIKA

PATENT KANTOOR
DEPARTEMENT VAN HANDEL
EN NYWERHEID



REPUBLIC OF SOUTH AFRICA

PATENT OFFICE
DEPARTMENT OF TRADE AND
INDUSTRY

Hiermee word gesertifiseer dat
This is to certify that

REC'D 18 OCT 2004

WIPO PCT

1. South African Provisional Patent Application No. 2003/6316 accompanied by a Provisional Specification was originally filed at the South African Patent Office on **14 August 2003**, in the name of **RAND AFRIKAANS UNIVERSITY** in respect of an invention entitled: "**A METHOD FOR PREPARING A SEMICONDUCTOR FILM OF A GROUP 1-111-V1 QUARTERNARY OR HIGHER ALLOY**".
2. The photocopy attached hereto is a true copy of the provisional specification and drawings filed with South African Patent Application No. 2003/6316.

Geteken te
PRETORIA

in die Republiek van Suid-Afrika, hierdie
in the Republic of South Africa, this

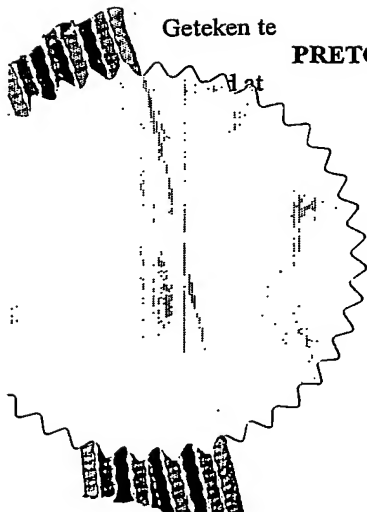
8

dag van
September 2004
day of

.....
Registrar of Patents

**PRIORITY
DOCUMENT**

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)



REPUBLIC OF SOUTH AFRICA

PATENTS ACT, 1978

REGISTER OF PATENTS

OFFICIAL APPLICATION NO.		LODGING DATE : PROVISIONAL		ACCEPTANCE DATE	
21	04	2003/6316		22	14 August 2003
INTERNATIONAL CLASSIFICATION		LODGING DATE : COMPLETE		GRANTED DATE	
51		23			

FULL NAME(S) OF APPLICANT(S) / PATENTEE(S)

71 RAND AFRIKAANS UNIVERSITY

APPLICANTS SUBSTITUTED :

71

DATE REGISTERED

ASSIGNEE(S)

71

DATE REGISTERED

FULL NAME(S) OF INVENTOR(S)

72 ALBERTS, Vivian

PRIORITY CLAIMED

COUNTRY

NUMBER

DATE

N.B. Use international
abbreviation for country.
(See Schedule 4)

33

31

32

TITLE OF INVENTION

54 A METHOD FOR PREPARING A SEMICONDUCTOR FILM OF A GROUP I-III-VI QUARTERNARY OR HIGHER ALLOY

ADDRESS OF APPLICANT(S) / PATENTEE(S)

Kingsway & University Road
Auckland Park
2006
South Africa

ADDRESS FOR SERVICE

REF

74 D M Kisch Inc, 54 Wierda Road West, Wierda Valley, SANDTON

P27103ZA00

PATENT OF ADDITION NO.

DATE OF ANY CHANGE

61

FRESH APPLICATION BASED ON

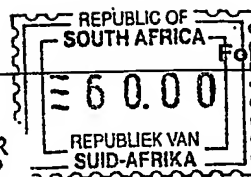
DATE OF ANY CHANGE

REPUBLIC OF SOUTH AFRICA
PATENTS ACT, 1978

APPLICATION FOR A PATENT AND ACKNOWLEDGEMENT OF RECEIPT
(Section 30 (1) - Regulation 22)
The grant of a patent is hereby requested by the undermentioned applicant
on the basis of the present application filed in duplicate.



P31HR
229



OFFICIAL APPLICATION NO	
21	01 2003/6316

DMK REFERENCE
P27103ZA00

FULL NAME(S) OF APPLICANT(S)

71	RAND AFRIKAANS UNIVERSITY
----	---------------------------

ADDRESS(ES) OF APPLICANT(S)

Kingsway & University Road Auckland Park 2006 South Africa

TITLE OF INVENTION

54	A METHOD FOR PREPARING A SEMICONDUCTOR FILM OF A GROUP III-VI QUATERNARY OR HIGHER ALLOY		
	THE APPLICANT CLAIMS PRIORITY AS SET OUT ON THE ACCOMPANING FORM P2 The earliest priority claimed is		
	THIS APPLICATION IS FOR A PATENT OF ADDITION TO PATENT APPLICATION NO.	21	01
	THIS APPLICATION IS FRESH APPLICATION IN TERMS OF SECTION 37 AND BASED ON APPLICATION NO.	21	01

THIS APPLICATION IS ACCOMPANIED BY :			
--------------------------------------	--	--	--

x	1a	A single copy of a provisional specification of 42 pages.
	1b	Two copies of a complete specification of pages.
	2a	Informal drawings of sheets.
x	2b	Formal drawings of 7 sheets.
	3	Publication particulars and abstract (form P8 in duplicate).
	4	A copy of figure of the drawings for the abstract.
	5	Assignment of invention (from the inventors) or other evidence of title.
	6	Certified priority document(s).
	7	Translation of priority document(s).
	8	Assignment of priority rights.
	9	A copy of form P2 and a specification of S.A. Patent Application.
	10	A declaration and power of attorney on form P3.
	11	Request for ante-dating on form P4.
	12	Request for classification on form P9.
	13a	Request for delay of acceptance on form P4.
	13b	

21 01

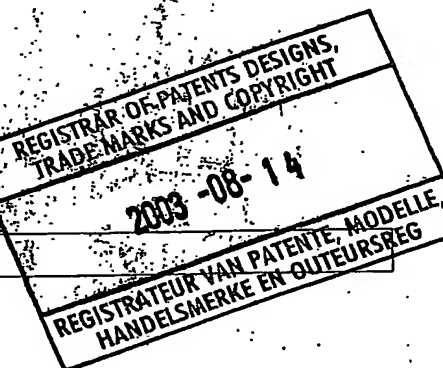
DATED 14 August 2003

Patent Attorney for Applicant(s)

ADDRESS FOR SERVICE	
74	D M Kisch Inc Inanda Greens Business Park 54 Wierda Road West Wierda Valley SANDTON

RECEIVED
OFFICIAL DATE STAMP
REGISTRAR OF PATENTS

The duplicate will be returned to the applicant's address for service as



REPUBLIC OF SOUTH AFRICA

PATENTS ACT, 1978

PROVISIONAL SPECIFICATION
(Section 30 (1) - Regulation 27)

OFFICIAL APPLICATION NO.		LODGING DATE	DMK REFERENCE
21	01 . 2003 / 6316	22 14 August 2003	P27103ZA00

FULL NAME(S) OF APPLICANT(S)	
71	RAND AFRIKAANS UNIVERSITY

FULL NAME(S) OF INVENTOR(S)	
72	ALBERTS, Vivian

TITLE OF INVENTION	
54	A METHOD FOR PREPARING A SEMICONDUCTOR FILM OF A GROUP I-III-VI QUARTERNARY OR HIGHER ALLOY

A method for preparing a semiconductor film of a group I-III-VI quaternary or higher alloy.

Field of the invention

5

THIS invention relates to a method for the preparation of a semiconductor film, and in particular a group I-III-VI quaternary or higher alloy semiconductor film.

10 Background to the invention

For the purposes of this specification the term "pentenary alloy" refers to an alloy having 5 different elements. So for example, $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ is a pentenary alloy wherein the 5 different
15 elements are copper (Cu), indium (In), gallium (Ga), selenium (Se) and sulfur (S). Similarly the term "quaternary alloy" refers to an alloy having 4 different elements. Likewise, a ternary alloy has three different elements and a binary alloy has two different elements.

20

Crystalline and multi-crystalline silicon is to date the primary material used in the production of solar modules/photovoltaic cells. The main problem associated with this material is the high cost of manufacturing. In an effort to reduce fabrication costs and
25 increase material utilization, semiconductor thin film alloys have

been the subject of intensive research. In this regard, group I-III-VI semiconductor films, such as CuInSe_2 and its alloys with CuGaSe_2 and CuInS_2 , are promising candidates for absorber layers in thin film photovoltaic cells or devices.

5

Of particular interest are group I-III-VI semiconductor films comprising Ga in combination with another group III element, since the presence of Ga in such films results in absorber films with higher band gap values and subsequently, in solar/photovoltaic cell devices, with higher open-circuit voltages and reduced short circuit currents. Of even greater interest is pentenary alloy semiconductor films.

In respect of pentenary alloy semiconductor films having $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)(\text{Se}_{1-y}\text{S}_y)_2$ as a general formula, the band gap can be shifted systematically between 1.0 and 2.4eV in order to achieve an optimum match with the solar spectrum. Optimization of this material system has already resulted in laboratory-scale solar cell devices with conversion efficiencies exceeding 18%.

20

Despite the interest in group I-III-VI semiconductor films that comprise Ga, methods of preparing such films have not been perfected. To date, the most successful method for preparing such films are:

25

(a) complex single-stage techniques in which all the elements (Cu, In, Ga, Se and / or S) are co-evaporated from individual sources. This technique allows for the controlled incorporation of gallium and sulfur into the films and hence the formation of homogeneous thin films.

However, the use of this technique has raised many critical questions about its acceptance as a commercially viable process due to large area uniformity problems and poor material utilization. (see M.E Beck, A. Swartzlander, R. Matson et al; Sol. Energy Mater. Sol. Cells; 64, 2000, 135.)

(b) two-step growth techniques, which involve (i) depositing of metallic thin films onto a substrate and (ii) the selenization and/or sulfurization of the metallic thin films in an Se and/or S containing atmosphere. These techniques are disclosed in an article by V. Alberts, J.H. Schön, and E. Bucher, Journal of Appl. Phys. 84(12), 1998, 6881 and by A. Gupta and S. Isomura, Sol. Energy Mater. Sol. Cells 53, 1998, 385.

Whereas the two step growth techniques are capable of commercial application, a number of problems have been encountered such as:

(i) there is poor adhesion of the resultant film to the substrate used to support the semiconductor film;

(ii) there is a reaction between Se and a metallic contact layer provided on the substrate, resulting in the formation of a highly resistive metallic back contact layer.

A further disadvantage with the two-step growth techniques is that the resultant films are heterogeneous. Without wishing to be bound by theory, and solely for the purposes of background, the selenization of thin film metallic precursors such as Cu, In and Ga results in the formation of the binary selenides such as CuSe, InSe and Ga₂Se₃. Carrying out the selenization reaction under the below prior art conditions results in the binary selenides reacting fully with each other to form discrete, ternary alloys such as CuInSe₂ and CuGaSe₂, therefore providing a heterogeneous semiconductor film.

Typically, these prior art conditions involve the reactive annealing of the metallic thin film containing Cu, In and Ga in a selenium-containing atmosphere at a single temperature of around 500°C, resulting in:

(a) segregated semiconductor films wherein the semiconductor film comprises two layers of CuInSe_2 and CuGaSe_2 ternary alloys (where the metallic film is slowly heated over a period of 20 minutes or longer to the reaction temperature, followed by annealing in H_2Se for at least 60 minutes); or

(b) a semiconductor film having a significant degree of inter-diffusion such that the Ga is graded throughout the film, the concentration of Ga increasing from the surface of the film towards the substrate (where the metallic film is heated rapidly within 5 minutes to the reaction temperature, followed by annealing in H_2Se for at least 60 minutes).

The open-circuit voltages (V_{oc}) and short circuit currents (J_{sc}) of solar modules/photovoltaic cells are directly related to the band gap of the semiconductor material. In the case of CuInSe_2 with a low band gap value of 1 eV, the V_{oc} values are typically limited to 500 mV, while values close to 1000 mV can be achieved using a CuGaSe_2 absorber layer with a higher band gap value of 1.65 eV.

In the case of segregated or graded film structure with most of the gallium residing at the back of the film, the absorber film exhibits a low band gap value in the active region of the photovoltaic cell, which ultimately limits the V_{oc} of the device. In addition, in the case of graded structures, lattice mismatches

within the graded absorber films introduce electrically active structural defects, which negatively impact on the device performance.

- 5 Once a heterogeneous $\text{Cu}(\text{In,Ga})\text{Se}_2$ structure is formed, converting the film to a homogeneous material becomes extremely difficult. In an effort to increase the band gap in the near-surface region of the absorber, films are commonly reacted with H_2S .

10

Present industrial processes include a post-sulfurization step in which a certain fraction of the selenium species are replaced with sulfur. (See the articles by K. Kushiya, M. Tachiyuki, T. Kase, I. Sugiyama, Y. Nagoya, D. Okumura, M. Satoh, O. Yamase, and H. Takeshita, *Sol. Energy Mater. Sol. Cells* **49**, 1997, 277; and R. Gay, M. Dietrich, C. Fredric, C. Jensen, K. Knapp, D. Tarrant and D. Willett, *Proceedings of the International Conference on E.C. Photovoltaic Solar Energy*, Vol. **12(1)**, 1994, 935.).

15

- 20 The above approach is hampered by the slow exchange process between the selenium and sulfur in these films, and it achieves only a slight increase in the open-circuit voltages of solar cell devices. This process also involves high temperatures and long reaction times of between 90 to 120 minutes, which ultimately

increases the costs of the process and often makes it commercially unviable.

It has also been demonstrated, in an article by M. Marudachalam,
5 R.W. Birkmire, H. Hichri, J.M. Schultz, A. Swartzlander and M.M.
Al-Jassim, J. Appl. Phys. **82**(6), 1997, 2896, that homogeneous
Cu(In,Ga)Se₂ thin films can be produced by annealing a phase-
separated mixture of CuInSe₂ and CuGaSe₂ in argon in the
temperature range of 500°C to 600°C for 60 to 120 minutes. This
10 post-annealing step in an inert atmosphere resulted in substantial
losses of Se from the film, which necessitated the re-introduction
of group VI elements.

It has now surprisingly been found by the inventor that the
15 significant problems discussed above can at least partially be
overcome or reduced by controlling the formation of the ternary
alloys in the selenization step such that the selenization reaction
does not proceed to completion thereby to form a stable mixture
of binary and ternary alloys.

20

Object of the Invention

It is an object of the invention to provide a novel alternative
process for the preparation of a group I-III-VI semiconductor film.

25

Disclosure of the Invention

A method for preparing a semiconductor film of a group I-III-VI quaternary or higher, the method comprising the steps of:

5

i. providing a metal film comprising a mixture of group I and group III metals;

10

ii. heat treating the metal film in the presence of a source of a first group VI element (hereinafter referred to as VI_1) under conditions to form a first film of a stable mixture of at least one binary alloy and at least one group I-III- VI_1 ternary alloy, the at least one binary alloy being selected from the group consisting of group I- VI_1 and group III- VI_1 alloys;

15

20

iii. optionally heat treating the first film in the presence of a source of a second group VI element (hereinafter referred to as VI_2) under conditions to convert the first film into a second film comprising at least one alloy selected from the group consisting of group I- VI_1 - VI_2 alloys and group III- VI_1 - VI_2 alloys; and the at least one group I-III- VI_1 ternary alloy of step (ii);

- iv. heat treating either the first film or second film to form a semiconductor film of a group I-III-VI quaternary or higher order alloy.

5 For the purposes of this specification the term stable shall be taken to mean that the molar ratio of the group I-VI₁ and/or group III-VI₁ species to the at least one group I-III-VI₁ ternary alloy remains substantially constant.

10 Step (i)

The metal film of step (i) may be provided on a substrate, which substrate is preferably inert under the reaction conditions and heat treatment steps of the above method. Suitable substrates
15 include glass, flexible metallic, polymer foils or the like. Preferably, the substrate is from 0.05 mm to 3.0 mm thick.

The substrate may optionally be coated with a metal layer, preferably a Mo layer having a thickness of 0.5 to 1.0 μm.
20 Preferably, the metal film is provided on the metal layer.

In a preferred embodiment of the invention, the metal film of step (i) comprises a mixture of metals selected from the group consisting of Cu, In and Ga, preferably a combination of Cu, In
25 and Ga, which metals may be in elemental form or in the form of

an alloy. Preferably the source of Cu and Ga is an alloy, preferably $\text{Cu}_{0.75}\text{Ga}_{0.25}$ alloy. Preferably the metal film is a Cu-In-Ga alloy. Other group III elements of interest in addition to Ga are Al and Th.

5

The metals may be deposited onto the substrate by techniques well known in the art, such as direct current (DC) magnetron sputtering, to form the metal film which may be 0.6 to 1 μm thick, preferably 0.6 μm thick. It will be appreciated that there are other
10 means by which the group I and group III metals may be deposited onto the substrate such as for example by means of electro-deposition or evaporation.

15 *Step (ii)*

The metal film of step (i) is heat treated in the presence of a source of a group VI₁ element. Preferably VI₁ is Se. More preferably the source comprises an atmosphere of H_2Se and
20 preferably at least one other gas, preferably an inert gas such as Ar. It is also envisaged that elemental Se in vapour form may also be used.

The molar concentration of Se relative to the at least one other
25 gas, preferably Ar, may be between 0.01 to 15 molar percent

preferably between 0.02 to 1.0 molar percent and more preferably between 0.05 to 0.3 molar percent.

In one embodiment of the invention step (ii) is carried out under
5 reaction conditions wherein the reaction temperature is between 300°C to 500°C, preferably between 350°C to 450°C.

In a preferred embodiment of the invention, the metal film of step
1 (i) is heated rapidly to the reaction temperatures set out above.
10 More preferably, the metal film is heated to the reaction temperatures set out above within 5 minutes.

Preferably, the metal film of step (i) is exposed to the source of the group VI₁ containing element for a period of between 10 to
15 120 minutes, preferably 15 to 90 minutes and more preferably between 30 to 60 minutes.

In one embodiment of the invention, the metal film of step (i) is heat treated in the presence of a source of Se to form a first film
20 comprising a stable mixture of binary selenides, comprising CuSe, InSe and Ga₂Se₃ and at least one group I-III-VI ternary alloy.

Preferably the first film is Se deficient in that the first film has
25 below 50 atomic % of Se. Preferably the first film comprises a Se

concentration of between 43 – 47 atomic %, relative to 50 atomic % required for stoichiometric fully reacted films. Preferably the Se/(Cu+Ga+In) ratio is below 1.

- 5 In a preferred embodiment of the method as defined above, the first film is subjected to a treatment step under conditions to ensure that the mixture of binary selenides and the at least one group I-III-VI ternary alloy remains stable.
- 10 Preferably, the conditions include the removal of the source of the group VI₁ element thereby to maintain the stability of the mixture. In a preferred embodiment, the conditions may also include the exposure of the first film to an inert atmosphere, preferably Ar, for a period of between 5 to 20 minutes, preferably
- 15 10 to 15 minutes. The first film may also be cooled, preferably to temperatures below 100°C.

Method for the formation of a group I-III-VI pentenary alloy semiconductor film.

20

Steps (i) and (ii) are as set out above.

Step (iii)

In one embodiment of the invention, the first film is heat treated in the presence of a source of a second group VI_2 element, preferably so as to convert the first film into a second film comprising a group I- VI_1 - VI_2 alloy; a group III- VI_1 - VI_2 alloy and the at least one group I-III- VI_1 ternary alloy.

Preferably VI_2 is a source of S. In a preferred embodiment of the invention, the source of S comprises a mixture of H_2S and at least one inert gas, preferably an inert gas such as Ar.

In a preferred embodiment of the invention, the molar concentration of S relative to the at least one inert gas, preferably Ar, may be between 0.1 to 10 molar percent, preferably between 0.3 and 0.5 molar percent.

The heat treatment of step (iii) may be at a temperature of between $100^{\circ}C$ to $500^{\circ}C$, preferably $400^{\circ}C$ to $500^{\circ}C$, more preferably $450^{\circ}C$ for a period of between 5 to 10 minutes, preferably 5 minutes.

In a preferred embodiment of the invention and where VI_1 in step (ii) is a source of Se, the second film may be subjected to the heat treatment of step (iii), wherein VI_2 is S, so as to convert the

first film to a second film comprising a mixture of sulfoselenides and the at least one group I-III-VI ternary alloy, the sulfoselenides being selected from the group consisting of Cu(Se,S), In(Se,S) and Ga(Se,S), preferably all three of them.

- 5 Preferably there are two Group I-III-VI₁ ternary alloys, preferably CuGaSe₂ and CuInSe₂.

Step (iv)

- 10 In a preferred embodiment of the invention, the second film of step (iii) may be annealed, preferably in the presence of a source of S, for a period of between 5 to 10 minutes, preferably 5 minutes at a temperature of between 450°C to 600°C, preferably 500°C to 550°C, more preferably 500°C, such that at least one
15 alloy selected from the group consisting of group I-VI₁-VI₂ and group III-VI₁-VI₂ alloys reacts with the at least one group I-III-VI₁ alloy to form at least one group I-III-VI quaternary alloy comprising either two group III metals or two group VI elements, namely VI₁ and VI₂.

20

Preferably the sulfoselenides react with the at least one group I-III-VI₁ ternary alloy, preferably with both group I-III-VI₁ ternary alloys of CuInSe₂ and CuGaSe₂ to produce a mixture of CuIn(Se,S)₂ and CuGa(Se,S)₂.

25

Preferably the resultant mixture is annealed for 15 to 90 minutes, more preferably 30 minutes to a temperature of between 500°C to 600°C, preferably 520°C to 580°C, more preferably at 550°C to form a pentenary alloy having the general formula I:

5



wherein preferably x may vary between 0.1 and 0.5, preferably
10 between 0.25 and 0.3 and y may preferably vary between 0 and 1, more preferably between 0.05 and 0.5.

The pentenary alloy is preferably a homogeneous film and may preferably be annealed for an additional 15 minutes to optimise
15 the structural properties of the pentenary alloy. The homogeneous film may be between 1.5 µm to 2.0 µm thick.

Method for the formation of a group I-III-VI quaternary alloy semiconductor film.

20

Step (i) and step (ii) are the same as discussed above and step (iii) is not carried out.

Step (iv)

In one embodiment of the invention, the first film of step (ii) is heat treated in an inert atmosphere, preferably an Ar containing atmosphere.

Preferably, the first film of step (ii) may be annealed in an Ar containing atmosphere at a temperature of between 100°C to 600°C, preferably between 200°C to 550°C, more preferably between 500°C and 550°C for 10 to 60 minutes, preferably between 15 and 30 minutes.

In a preferred embodiment of the invention, the first film is then annealed in the presence of a source of a Group VI₁ element, where VI₁ is preferably Se as in step ii. The first film is annealed preferably 10 to 60 minutes, more preferably 30 minutes to form a quaternary alloy, namely Cu(In,Ga)Se₂. Preferably the source of Se is an atmosphere of H₂Se and at least one other gas, preferably an inert gas such as Ar. Preferably the molar concentration of Se relative to the at least one other gas is 0.06%.

Preferably the quaternary alloy is homogeneous.

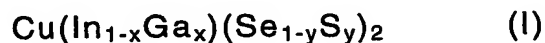
It is preferable when forming the quaternary alloy that step (ii) be carried out at a temperature of 350°C to 450°C; preferably 400°C such that the first film comprises a stable mixture of binary selenides, selected from the group consisting of CuSe, InSe and Ga₂Se₃; and a single ternary alloy, namely CuInSe₂.

According to a second aspect of the invention there is provided a method for the production of a group I-III-VI pentenary alloy semiconductor film comprising the steps of:

- (i) providing a metal film comprising a mixture of Cu, In and Ga on a substrate;
- (ii) heat treating the metal film in the presence of a source of Se under conditions to form a first film comprising a stable mixture of CuSe, InSe, Ga₂Se₃ and at least one ternary alloy selected from the group consisting of, CuInSe₂ and CuGaSe₂;
- (iii) heat treating the first film in the presence of a source of S under conditions to convert the first film into a second film comprising a mixture of sulfoselenides, namely Cu(Se,S), In(Se,S) and Ga(Se,S) and the at least one ternary alloy;

- (iv) heat treating the second film of step (iii) to react the said mixture to form a pentenary alloy of Cu, In, Ga, Se and S.

Preferably the pentenary alloy has the formula I:



5

10

preferably x may vary between 0.1 and 0.5, preferably between 0.25 and 0.3 and y may be between 0 and 1, preferably between 0.05 and 0.5.

15

The method according to the second aspect of the invention, wherein the first film is preferably subjected to a treatment step under conditions to ensure that the mixture of binary selenides and the ternary alloys remains stable.

20

According to a third aspect of the invention there is provided a method for the production of a group I-III-IV quaternary alloy semiconductor film comprising the steps of:

- (i) providing a metal film comprising a mixture of Cu, In and Ga on a substrate;

25

- (ii) heat treating the metal film in the presence of a source of Se under conditions to form a first film comprising a

stable mixture of binary alloys, and at least one ternary alloy, the binary alloys comprising CuSe, InSe and Ga₂Se₃, and the at least one ternary alloy being selected from the group consisting of CuInSe₂ and CuGaSe₂

5

- (iii) heat treating the first film of step (ii) to form an alloy of Cu, In, Ga and Se.

Preferably the quaternary alloy is Cu(In,Ga)Se₂.

10

The method according to the third aspect of the invention, wherein step (ii) is preferably carried out at a reaction temperature of about 400°C such that the first film comprises a stable mixture of the binary selenides and CuInSe₂.

15

Preferably the first film is subjected to a treatment step under conditions to ensure that the mixture of binary selenides and the ternary alloys remains stable.

Detailed Description of the Invention

Without thereby limiting the scope of the invention and by means of example only embodiments of the invention will now be described by means of the following examples. In the examples reference is made to the accompanying figures:

Figures 1.1 - 1.2 are X-ray diffraction spectra (Cu K_{α} radiation) of the first film formed according to step ii of example 1. More particularly figure 1.1 is an XRD pattern of the first film of sample 200250-a and figure 1.2 is an XRD pattern of the first film of sample 200251-a;

Figure 2 are X-ray diffraction spectra (Cu K_{α} radiation) depicting the crystalline nature of the resultant second film of sample 200251-a, which were formed according to steps iii and iv of example 1, illustrating the transitions from the ternary to the quaternary and pentenary alloy states;

Figures 3.1-3.2. are GIXRD patterns of the [112] peak positions of the homogeneous pentenary

alloys of samples 200251-a and 200250-a in comparative example 1, measured with Cu K_{α} radiation;

Figure 4

is a plot of open-circuit voltage (V_{oc}) for a number of photovoltaic cells having semiconductor absorber films of sample 200251-a as set out in example 2;

Figure 5.1-
5.2

are XRD patterns (Cu K_{α} radiation) of a graded quaternary alloy of comparative example 2 and a homogeneous quaternary alloy of comparative example 2;

Figure 6

are GIXRD patterns of the [112] peak position of the homogeneous quaternary alloy of comparative example 2. The correspondence in the lattice parameters as function of sample depth indicates that the film is homogeneous rather than compositionally graded;

Figure 7.1-

7.2

are X-ray fluorescence profiles depicting the in-depth composition properties of the graded quaternary alloy and homogeneous quaternary alloy of comparative example 2 respectively.

General Experimental Procedure

5 It is well known to those skilled in the art that photovoltaic cells include a substrate for supporting a semiconductor film. Typically, any suitable substrate may be used, which substrate does not react with the semiconductor film and which does not modulate the semiconductor properties. Suitable substrates include glass,
10 flexible metallic or polymer foils and the like.

The substrate may have a thickness of 0.05 to 3.0 mm and is often coated with a metal layer of molybdenum in order to enhance the adhesion of a resultant semiconductor film to the
15 substrate and to serve as a contact in a completed photovoltaic device.

The thickness of the Mo coating is usually between 0.5 to 1.0 μm and is deposited onto the substrate by DC magnetron sputtering

at a working pressure of between 0.1 to 0.8 Pa. It will be appreciated that there are many other techniques known in the art which relate to the use and deposition of metal layers, for example there may be more than one layer, or chromium may be
5 used in place of molybdenum.

Step (i) of the method according to the invention

For purposes of the experiment, a 2 mm thick soda lime glass
10 substrate was used. The substrate was cleaned in an ultrasonically stirred soap solution for 10 minutes by gently moving the substrate placed in a holder. The substrate was then held under a cold deionised water tap for a few minutes to ensure the removal of excess soap thereon. Thereafter, the substrate
15 was cleaned in an ultrasonically stirred deionised hot water bath by gently moving the substrate holder. Finally, the substrate was dried for 10 minutes in dry-nitrogen in an oven maintained at 120°C.

20 Once dried, a Mo layer was deposited onto the substrate. This was followed by co-sputtering the metal film of Cu, Ga and In onto the Mo layer. The deposition of Mo and the co-sputtering were carried out in a DC magnetron sputtering unit consisting of a deposition chamber which accommodates three 9 inch circular
25 cathodes (targets): Mo, pure In and a $\text{Cu}_{0.75}\text{Ga}_{0.25}$ alloy target.

The deposition chamber was evacuated to a base pressure of 5×10^{-5} Pa for at least three hours. The Mo layer was deposited without any intentional heating of the substrate at a working pressure of 0.5 Pa, using Ar as plasma gas. The total thickness of the Mo layer was 1 μm .

The deposition of the Mo layer was followed, without breaking vacuum, by the co-sputtering of $\text{Cu}_{0.75}\text{Ga}_{0.25}$ and In at a working pressure of 0.3 Pa. The co-sputtering was also carried out without intentional substrate heating and the substrate was rotated during co-sputtering in order to enhance the mixing of the Cu-Ga-In alloy. The total thickness of the Cu-In-Ga alloys was 0.6 μm and the Cu/(In+Ga)- and Ga/(Ga+In)- atomic ratios were maintained at 0.9 and 0.25 respectively.

Example 1: Experimental procedure for the production of a group

I-III-VI pentenary alloy

Step ii of the method according to the invention

The substrate with the co-sputtered metal film of step i was placed in a horizontal quartz tube reactor (herein after referred to as the reactor tube). The substrate was laid on a graphite substrate holder and placed in the reactor tube. Graphite

substrate holders were used to ensure the uniform heating of the substrate.

The reactor tube was evacuated to a pressure of 2.67×10^{-4} Pa for at least two hours before carrying out step ii. The reaction tube was then pressurised and a constant Ar flow of 1300 standard cubic centimetres per minute (hereinafter referred to as sccm) was established and maintained during the reaction process.

Once a constant inert gas flow was established, the temperature of the substrate with the metal film was ramped up to the reaction temperatures set out in Table 1 below over a period of 5 minutes. The reaction gas mixture (0.06 molar % H_2Se in Ar) was passed through the reactor tube while the substrate was heated to the reaction temperatures set out in Table 1 for the reaction periods also set out in Table 1 so as to form a first film comprising a stable mixture of binary selenides, namely CuSe , InSe and Ga_2Se_3 and at least one of the following ternary alloys, namely CuInSe_2 and CuGaSe_2 . The presence of one or both of the ternary alloys is dependent upon the reaction temperature of step ii.

Referring to figure 1.1 which is an XRD pattern of the first film of step ii prepared under the reaction conditions set out in Table 1 for sample 200250-a, it is clear that there is present a mixture of

the three binary selenides and CuInSe_2 . Under the reaction conditions for sample 200250-a, there is no evidence of the formation of CuGaSe_2 at 400°C .

- 5 Referring to figure 1.2 which is an XRD pattern of the first film of step ii prepared under the reaction conditions set out in Table 1 below for sample 200251-a, reflections [112], [220/204] and [312/116] comprise (a) relatively sharply defined peak positions corresponding to CuInSe_2 and (b) shoulders resulting from the
10 presence of CuGaSe_2 and the remaining binary selenides of CuSe and Ga_2Se_3 .

Upon the termination of the reaction periods as set out in Table 1, the samples were subjected to a treatment step in order to further
15 maintain the stability of the resultant stable mixture. This was done by terminating the flow of H_2Se in the reaction tube and by rapidly cooling the samples to temperatures of below 100°C . The samples were kept under the above conditions for 15 minutes to ensure the complete removal of the H_2Se species from the reactor
20 tube.

Both figures 1.1 and 1.2 depict a stable mixture wherein the reaction conditions set out in Table 1 below prevent the reaction going to completion and thus forming fully reacted ternary alloys

of CuInSe_2 and CuGaSe_2 in the absence of CuSe , InSe and Ga_2Se_3 .

5 It is believed by the inventor that starving the system of Se by using extremely low concentrations of Se, and by using low temperatures so as to prevent the completion of the selenization reaction to form fully reacted ternary alloys, stable mixtures such as those represented in figures 1.1 or 1.2 can be achieved.

10 Table 1: Reaction conditions (temperature and time) for step ii according to the invention.

Reaction conditions	
Sample	($\text{H}_2\text{Se}/\text{Ar}$)
200248-c	400°C/20min
200250-a	400°C/30min
200263-a	400°C/40min
200371-a	400°C/60min
200251-a	450°C/30min

Step iii according to the method of the invention

15

The first film of step ii formed under the reaction conditions in Table 1 above was then heated in the reaction tube in an atmosphere containing a mixture of H_2S and Ar (the molar percentage of S in the reactive mixture being maintained close to

0.35% relative to Ar) at a reaction temperature of 450°C for a period of 5 minutes such that the binary selenides react with S to convert the first film of step ii into a second film comprising a mixture of sulfoselenides, namely Cu(Se,S), In(Se,S) and Ga(Se,S) and the ternary alloys.

Referring to Figure 2 which is a XRD pattern of sample 20051-a, and in particular the XRD for step iii, the presence of In(Se,S) is visible, however the remaining sulfoselenides of Cu(Se,S) and Ga(Se,S) are not shown in the selected 2θ range. The inventor believes that at temperatures around 450°C, and as depicted in the XRD for step iii, the reaction between the existing S species in the gaseous atmosphere and the ternary alloys (indicated by peaks 1 at 26.71° and 2 at 27.75° in fig. 2) is substantially insignificant. In other words, the reaction between S and the ternary alloys is insignificant at this specific temperature.

Step iv according to the method of the invention

The second film of step iii was then subjected to the following heat treatment steps in the reaction tube:

- (a) annealing the second film of step iii at temperatures of about 500°C for 5 minutes, such that the sulfoselenides react with the ternary alloys to produce quaternary

CuIn(Se,S)₂ and CuGa(Se,S)₂ alloys (indicated by peaks 3 at 27.01° and 4 at 28.05° in the XRD for step iv(a)).

5 It is believed by the inventor that in the event that step ii is carried out at 400°C, and thus in the absence of CuGaSe₂, the sulfoselenides may directly react to form CuGa(Se,S)₂ in this step. However, under the latter experimental conditions the resulting quaternary alloy will contain a higher S concentration, resulting in a shift of peak 4 to a
10 higher 2θ value than that indicated in the XRD pattern for step iv(a).

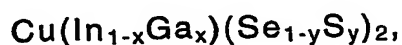
The reaction of S with the group I-III-VI₄ ternary alloys is represented by the absence of the sulfoselenides for
15 example, the absence of the In(Se,S) peak in the XRD pattern for step iv(a) in figure 2 is indicative of the fact that it has reacted with CuInSe₂ to form CuIn(Se,S)₂.

20 Comparing the XRD for step iii in figure 2 with the XRD for step vi(a) in figure 2, it is clear from the subsequent 2θ shift that the ternary alloys (represented by [112] peaks 1 and 2) have reacted with the sulfoselenides to form the quaternary alloys CuIn(Se,S)₂ and CuGa(Se,S)₂ (represented by [112] peaks 3 and 4).

The degree of shift of the [112] peak from position 1 to 3, and 2 to 4, is determined by the volume fraction of sulfoselenides available to react with the ternary alloys. The volume fraction sulfoselenides is in turn dependent on the volume fraction binary selenides present in the first film of step ii. Once the stable fully reacted quaternary alloys are formed around 500°C, the reaction process becomes diffusion limited and further reaction to H₂S/Ar at 500°C for extended periods has insignificant influences on the crystalline state and S content of the composite alloy.

(b) Annealing the resultant composite alloy in the reaction tube from (a) above at a temperature of 550°C for a period of 15 minutes. The transition from the quaternary to pentenary alloy state (indicated by peak 5 at 27.2° in the XRD for step iv(b) in Fig. 2) occurs within 10 to 15 minutes of the reaction with H₂S, while an additional 15 minutes of annealing is typically required to optimize the structural properties of the pentenary alloy.

The homogeneous pentenary alloys have typical thickness of between 1.5 and 2 μm and may be described by the chemical formula:



wherein x may vary between 0.1 and 0.5, preferably between 0.25 and 0.3 and y may be between 0 and 1, preferably between 0.05 and 0.5.

5

Both steps iii and iv are carried out consecutively in a reactive gas mixture of H_2S , wherein the temperature is ramped up from 450°C to 550°C.

10 Upon the completion of both steps iii and iv, the reaction tube was evacuated to a pressure of 2.67×10^{-4} Pa for at least two hours to ensure the complete removal of toxic gases from the reactor tube. The tube was then pressurized and the samples were removed.

15

Comparative Example 1 – pentenary alloys

The samples set out in Table 1 above were subjected to steps iii
20 and iv to form homogeneous semiconductor pentenary alloys and their corresponding chemical compositions as determined by energy dispersive x-ray spectroscopy (EDS) with reference to $Cu/(In+Ga)$, $Ga/(Ga+In)$, and $S/(Se+S)$ atomic ratios are set out in Table 2 below. Also shown in Table 2 below are the band gap
25 values for each of the samples as well as the position of the [112] diffraction peaks.

Table 2: Summary of reaction conditions[†] and their influence on the degree of sulfur incorporation and the resulting band gap values of the respective samples.

Sample	Step II reaction condition s H ₂ Se/Ar	Step IV reaction conditions H ₂ S/Ar	Cu/In+Ga	Ga/Ga+In	S/Se+S	2 $\theta_{(112)}$	E _g (eV)
200248-c	400°C/ 20min	550°C/ 30min	0.90	0.25	0.56	27.65	1.39
200250-a	400°C/ 30min	550°C/ 30min	0.91	0.25	0.45	27.55	1.32
200263-a	400°C/ 40min	550°C/ 30min	0.90	0.25	0.32	27.30	1.23
200371-a	400°C/ 60min	550°C/ 30min	0.93	0.25	0.10	27.0	1.15
200251-a	450°C/ 30min	550°C/ 30min	0.92	0.24	0.23	27.20	1.20
200252-a	450°C/ 30min	550°C/ 90min [‡]	0.91	0.23	0.25	27.21	1.21

5

[†]These studies were conducted in a constant flow of 0.06% H₂Se diluted in Ar and 0.35% H₂S diluted in Ar. The 2 θ - positions of the [112] peaks of the pentenary alloys were measured by GIXRD with a Cu tube at 40kV. The corresponding band gap values were calculated from quantum efficiency measurements. [‡] The time period for step vi(b) was increased to 90 minutes.

10

A comparison of the first four samples in Table 2 clearly indicates the influence of the conditions of step ii of the invention on the

degree of sulfur incorporation which is set out in the S/(S+Se) column of the table. Accordingly, changing the conditions of step ii modified the subsequent reaction kinetics during step iii of the invention resulting in a change in the sulfur incorporation in the
5 final $\text{Cu}(\text{In}_{0.75}\text{Ga}_{0.25})(\text{Se}_{1-y}\text{S}_y)_2$ semiconductor film.

A comparison of sample # 200250-a and # 200251-a, indicates how an increase in the reaction temperature of step ii from 400°C to 450°C led to a substantial decrease in the sulfur incorporation
10 and hence a shift in the [112] diffraction peak to a lower angle.

In the case of the last two samples, (i.e. 200251-a and 200252-a) the reaction conditions of step ii were maintained constant, while the reaction periods for annealing the resultant composite alloy in
15 step iv(b) above was increased from 30 to 90 minutes. Comparison of these samples clearly indicates that annealing in the presence of an $\text{H}_2\text{S}/\text{Ar}$ atmosphere for extended periods above 30 minutes had marginal influences on the degree of sulfur incorporation.

20

Accordingly this indicates that the pentenary alloy is formed after only 30 minutes of annealing in $\text{H}_2\text{S}/\text{Ar}$ at 550°C therefore implying that once the fully reacted homogeneous pentenary alloys are produced, the reaction process becomes diffusion

limited and further incorporation of sulfur needs to occur via the replacement of selenium species.

Figures 3.1 and 3.2 are grazing-incidence x-ray diffraction (GIXRD) patterns of the [112] reflections of samples 200251-a, 200250-a set out in Table 2 above. In this characterization method, decreasing amounts of the incident angle result in a decreasing penetration depth of the x-ray beam. It is important to note that scattering angles between 0.2° and 10° revealed virtually no shift in the lattice parameters between the surface and bulk material, which confirms the homogeneity of the pentenary alloys. Of equal significance is that the variation in the conditions of step ii resulted in a dramatic shift in the 2θ - position of the [112] diffraction peaks. Since the gallium content is virtually constant in all composite alloys, this relative shift is attributed to the varying degrees of sulfur incorporation.

Example 2: Determination of the open-circuit voltages for various solar cell devices comprising homogeneous pentenary alloys as absorber films.

Solar cells devices were fabricated according to a standard cell fabrication procedure, which included a 50 nm CdS buffer layer and a 50 nm intrinsic ZnO/150 nm indium tin oxide (ITO) window layer. The glass/Mo/Cu(In,Ga)(Se,S)₂/CdS/ZnO cell structures

were evaluated under simulated A.M. 1.5 conditions at 25°C. The band gap values of the homogeneous pentenary alloys were varied by modifying the reaction conditions of step ii, as indicated in Table 2. The corresponding cell parameters are set out in Table 3 below.

Table 3: Summary of the cell parameters of various photovoltaic devices in which the absorber films are homogeneous pentenary alloys with different band gap values.

Samples	Ga/Ga+In	S/Se+S	E _g eV	V _{oc} mV	J _{sc} mA/cm ²	FF %	η %
200248-c	0.25	0.56	1.39	677.9	23.55	53.3	8.5
200250-a	0.25	0.45	1.32	685.9	27.17	59.8	11.2
200252-a	0.23	0.25	1.21	630.2	29.46	64.1	11.9
200251-a	0.24	0.23	1.20	610.4	32.86	67.5	13.5

The conversion efficiencies were critically related to the band gap of the pentenary alloys and varied between 8% and 14%, the best device being that with the lowest band gap (sample 200251-a). All devices had open-circuit voltages (V_{oc}) beyond 600 mV. Also, 24 photovoltaic cells were made from pentenary alloys prepared under the reaction conditions set out above for sample 200251-a. The V_{oc} values of these cells were confined to values in the range of 600 to 640 mV (see fig. 4). This is clear evidence of the reproducibility of the method according to the invention.

Example 3: Experimental procedure for the production of a group

I-III-VI quaternary alloy

Step i is the same as set out under general experimental
5 procedure.

Step ii of the method according to the invention

In this case the same method as set out in step ii above was
10 followed, however the reaction temperature was kept at 400°C so
as to form a first film comprising a stable mixture of binary
selenides and CuInSe_2 only.

It is believed by the inventor that in the case of the production of
15 quaternary alloy semiconductor films it is necessary to prevent
the formation of the second ternary alloy, namely CuGaSe_2 so as
to obtain a homogeneous quaternary alloy. This was achieved by
keeping the reaction temperature at 400°C.

20 As above, the first film of step ii is subjected to a treatment step
to maintain the stability of the mixture, wherein the H_2Se flow is
terminated and the first film is cooled to temperatures below
100°C. The Ar flow in this case was maintained for a period of at
least 15 minutes, once again to ensure the complete removal of
25 the H_2Se species.

Step iii of the method according to the invention

In the case of the production of a quaternary alloy semiconductor film, this step is not carried out.

5

Step iv of the method according to the invention

The first film is subjected to the following consecutive steps:

- 10 (a) heating the first film in the reaction tube in an inert atmosphere of Ar to a reaction temperature of 500°C for 5 minutes ;
- (b) annealing the first film in the reaction tube in an Ar containing atmosphere at 500°C for at least 15 minutes;
- 15 (c) annealing the first film in the presence of 0.06 molar percent of H₂Se in Ar for 30 minutes at 500°C
- 20 to form a homogeneous quaternary alloy semiconductor film.

As in the case of the formation of a pentenary alloy, the reaction tube was evacuated to a pressure of 2.67×10^{-4} Pa for at least two hours to ensure the complete removal of toxic gases from the

reactor tube. The tube was then pressurized and the samples were removed.

Comparative Example 2 – quaternary alloys

5

Figures 5.1 and 5.2 represent XRD patterns, depicting the crystalline features of a typical graded quaternary alloy and a homogeneous quaternary alloys respectively, the alloys being prepared in the manner set out below. In both cases,
10 measurements were taken with Cu K_{α} radiation at 40kV.

In the case of the graded quaternary alloy (see XRD pattern in Fig. 5.1), the alloy was rapidly heated in less than 5 minutes to 500°C in the presence of H_2Se , followed by an annealing step in 5
15 molar percent H_2Se in Ar for 60 minutes at 500°C. This procedure resulted in a significant degree of interdiffusion between the In-rich and Ga-rich phases and XRD analysis indicated the presence of a graded $CuIn_xGa_{1-x}Se$ structure. This phenomenon is represented by the asymmetric broadening of [112], [220/204] and
20 [312/116] diffraction peaks. In this regard it is important to note that the position of the [112] diffraction peak at 26.65° still represents the lattice parameters of the pure $CuInSe_2$ phase, while the shoulder is due to increasing amounts of Ga which extend all the way to the peak position of $CuGaSe_2$. It is therefore
25 reasonable to assume that the surface of the absorber film

contains pure CuInSe_2 and that the gallium increases gradually towards the Mo back contact.

The second sample, i.e. the homogeneous quaternary alloy, was prepared under the described experimental conditions set out in steps i, ii and iv for quaternary alloys. In order to control the reaction velocities of the binary selenides, step ii was carried out at 400°C , using extremely low gas concentrations of 0.06 molar % H_2Se in Ar. The reaction period was fixed at 30 minutes. After complete removal of Se species from the reaction zone, the first film was annealed in the presence of Ar for 15 minutes at a temperature of 500°C , followed immediately by an annealing step in 0.06 molar percent H_2Se in Ar for 30 minutes.

XRD studies of the homogeneous quaternary alloy, which is represented by Fig. 5.2, revealed that the resultant film was single-phase with no evidence of segregated material. The sharp, well-defined chalcopyrite peaks are indicative of high crystalline quality. It is also important to note that the [112] peak position increased from about 26.65° , which is typical for pure CuInSe_2 (as shown in Figure 5.1), to a 2θ value of 26.95° . The latter shift of the chalcopyrite reflection towards a larger 2θ value is in accordance with a decrease in the lattice parameter associated with an increase in Ga content in the quaternary system. This degree of shift of the diffraction peaks towards higher 2θ values

is exactly in accordance with Vegard's law, assuming single-phase material and a Ga/(Ga+In) atomic ratio close to 0.25.

Figure 6 depicts GIXRD patterns of the [112] peak of the homogeneous quaternary alloy at incident angles between 0.5° and 10°. Once again it should be realized that a decrease in the incident angle results in a decrease in penetration depth of the x-ray beam. It is important to note from Fig. 6 that scattering angles between 0.5° and 10° revealed virtually no shift in the lattice parameters between the surface and bulk material, which confirms that the film is uniform rather than compositionally graded.

The in-depth compositional features of the quaternary alloys were studied by x-ray fluorescence (XRF). In this characterization method, the quaternary alloys were repeatedly etched in bromine methanol, followed by XRF $K_{\alpha 1,2}$ line intensity measurements of the remaining material after each etching step. From these analyses the chemical compositions of the graded film and homogeneous films represented in Fig 5.1. and Fig 5.2 could be estimated through almost the entire film thickness.

Figure 7.1 represents the in-depth compositional uniformity of the compositionally graded $\text{CuIn}_{0.75}\text{Ga}_{0.25}\text{Se}_2$ alloys film of Fig 5.1. It is important to note from Fig. 7.1 that the Cu and Se element

concentrations remained virtually constant through the entire thickness of the film. Even more significant, it can be seen that the remaining material after the successive etching steps became increasingly gallium-rich, while an opposite trend was observed for indium. The resulting Ga/(Ga+In) atomic ratio increased from a value of 0.28 for the sample before etching to 0.75 after the last etching step. This continuous increase in the Ga/(Ga+In) atomic ratio with sample depth is consistent with the graded $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ phase observed by the XRD studies in Fig. 5.1.

Figure 7.2 represents the in-depth compositional properties of the homogeneous film. It can be seen that the Cu, In, Ga and Se concentration remained virtually constant through the entire layer thickness of these specific quaternary alloys. These results are therefore in line with the XRD data presented in Fig. 5.2, confirming that this growth process eliminated the grading of gallium and indium in the $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ phase and resulted in a homogeneous quaternary alloy.

The above are only embodiments of the invention and it will be appreciated that many variations in detail are possible without thereby departing from the scope and spirit of the invention.

Dated this 14 day of August 2003


Patent Attorney / Agent for the Applicant

2003/6316

Figure 1.1

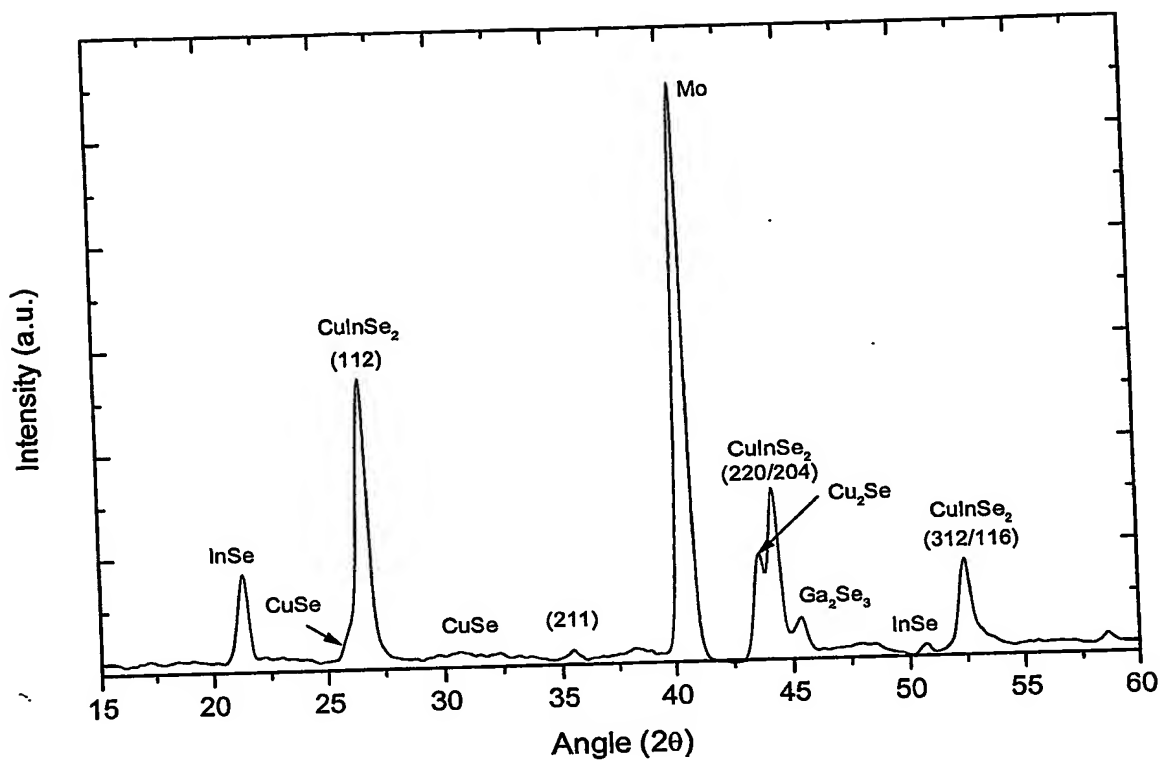


Figure 1.2

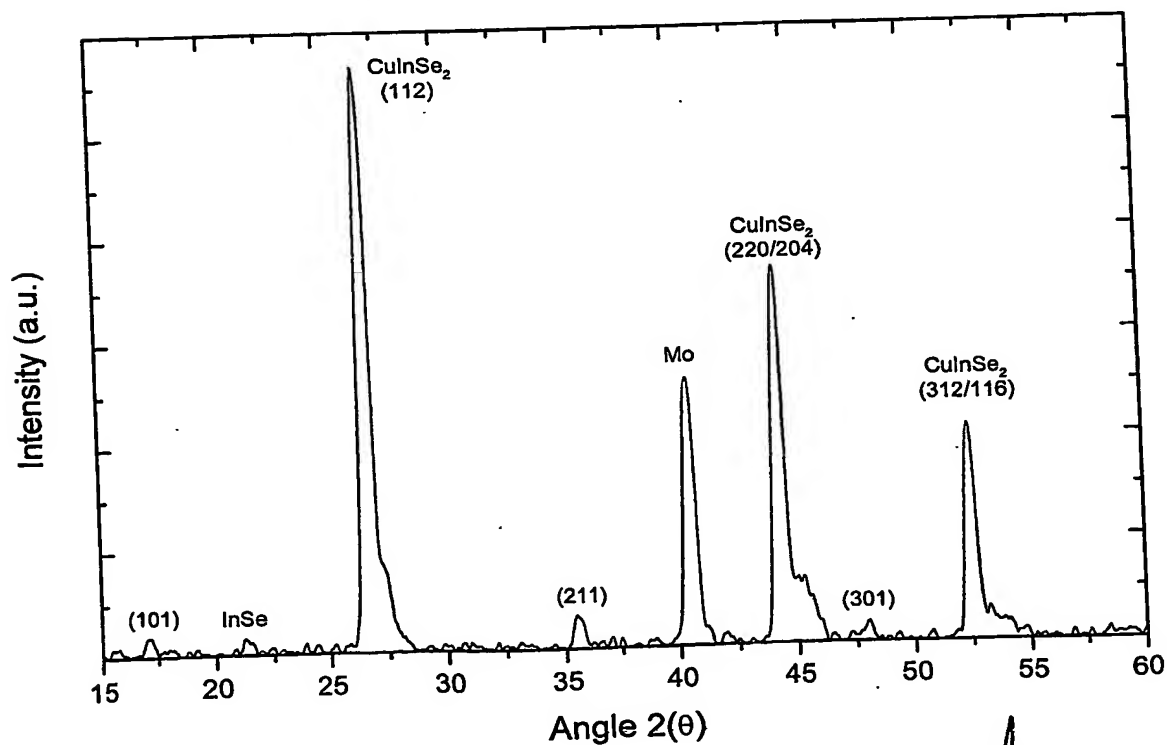


Figure 2

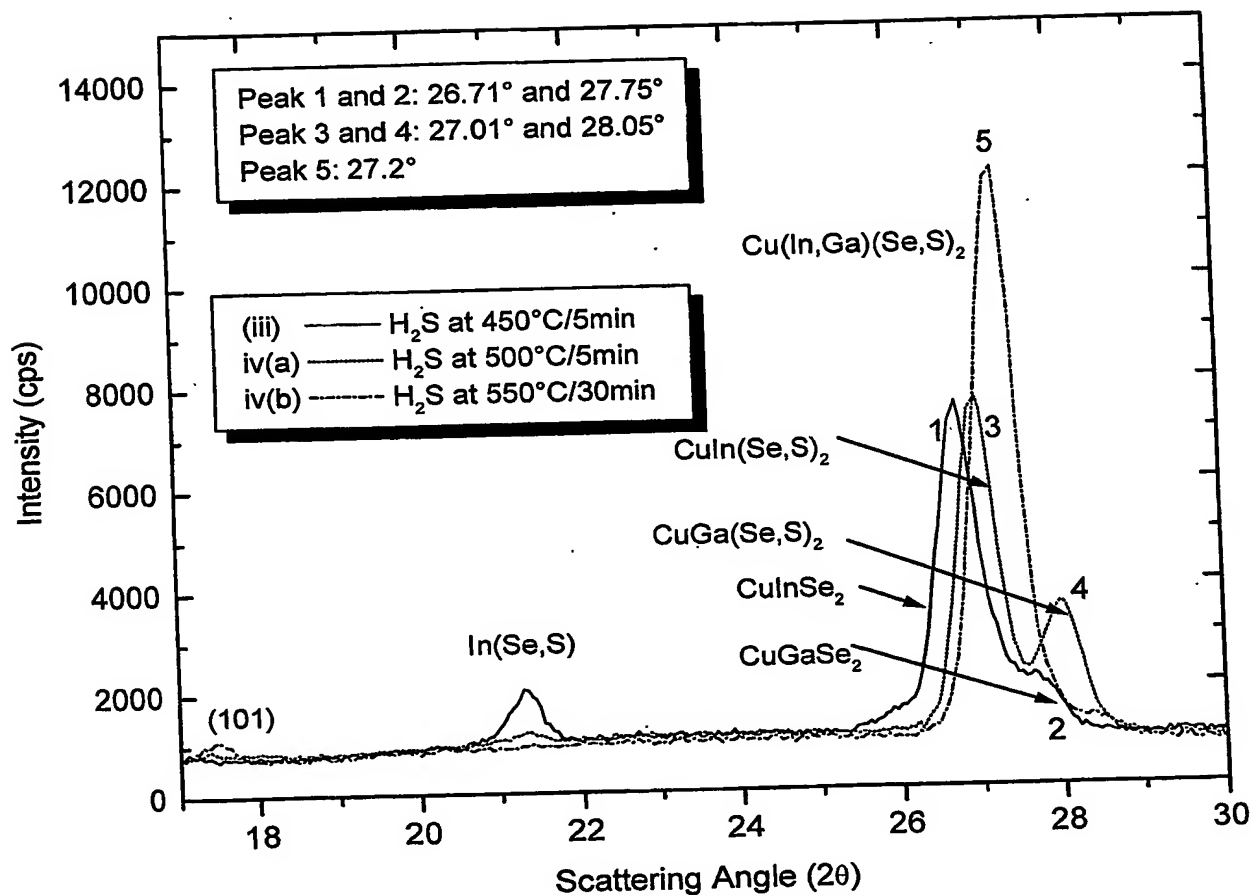


Figure 3.1

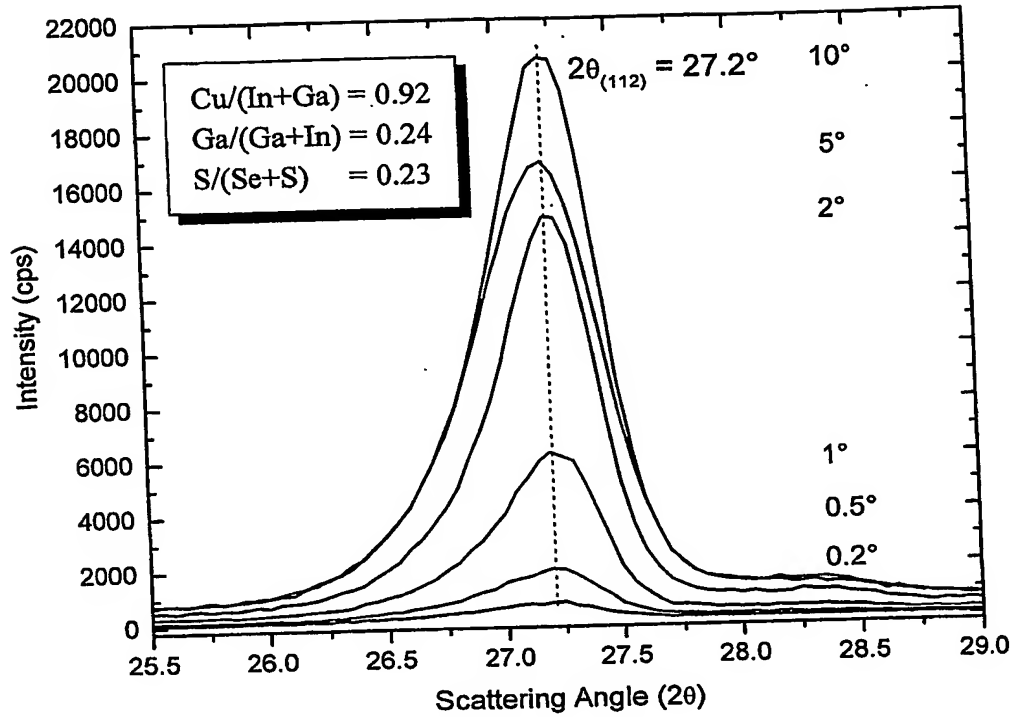
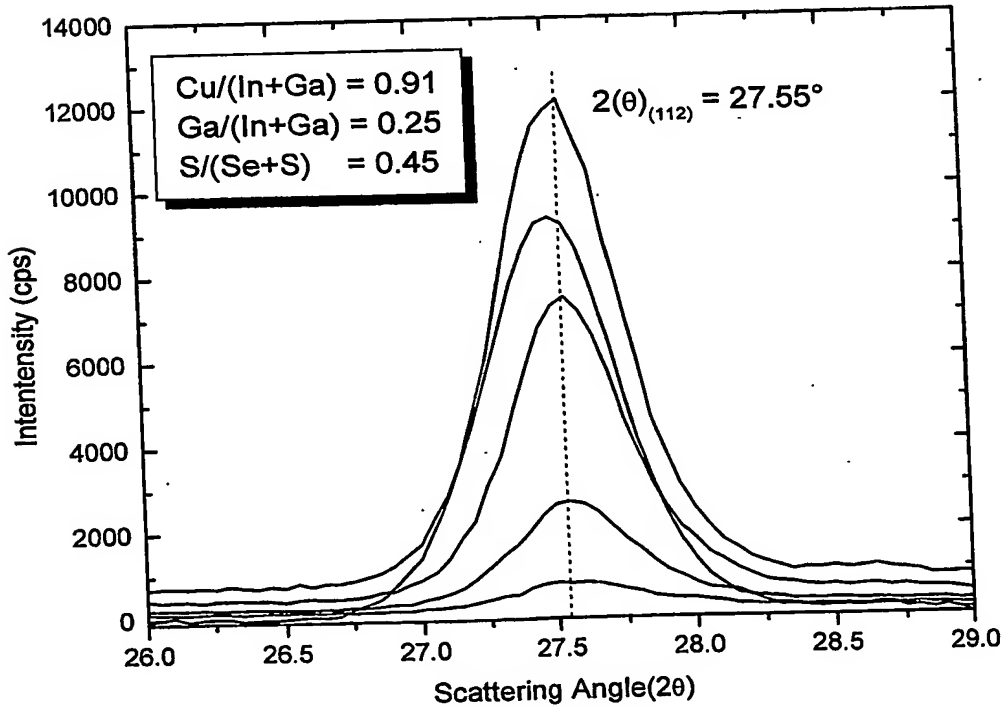


Figure 3.2



2003/6316

Figure 4

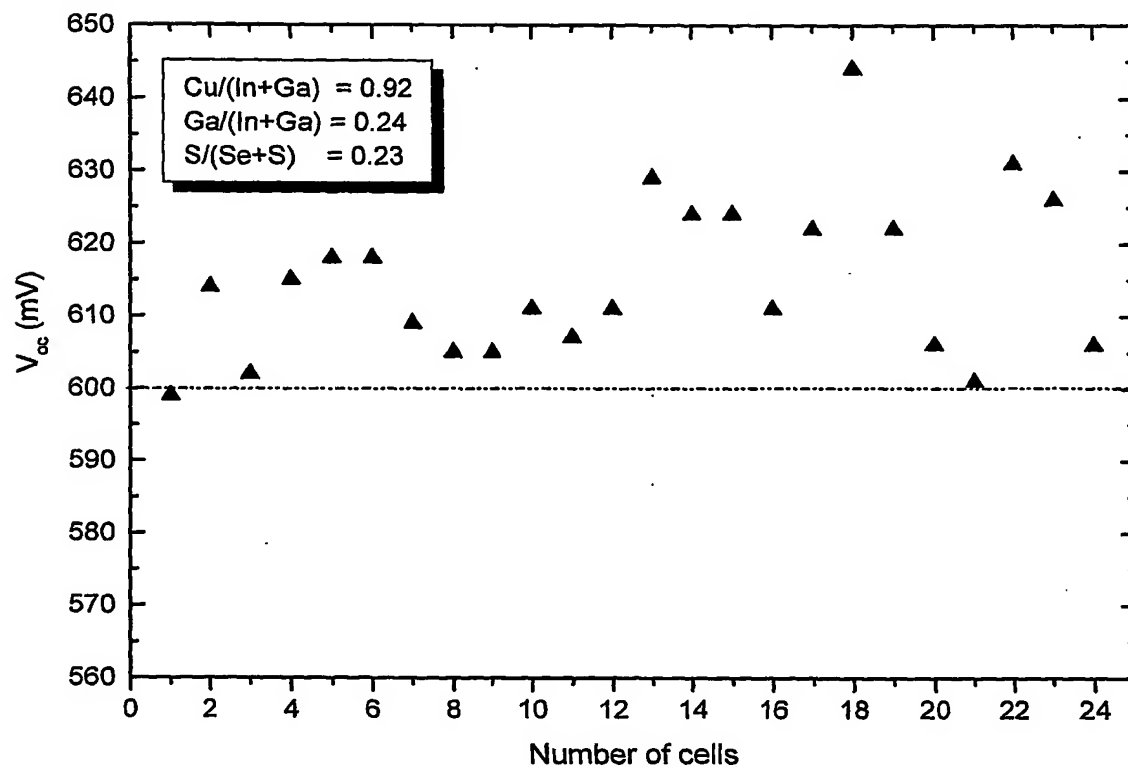


Figure 5.1

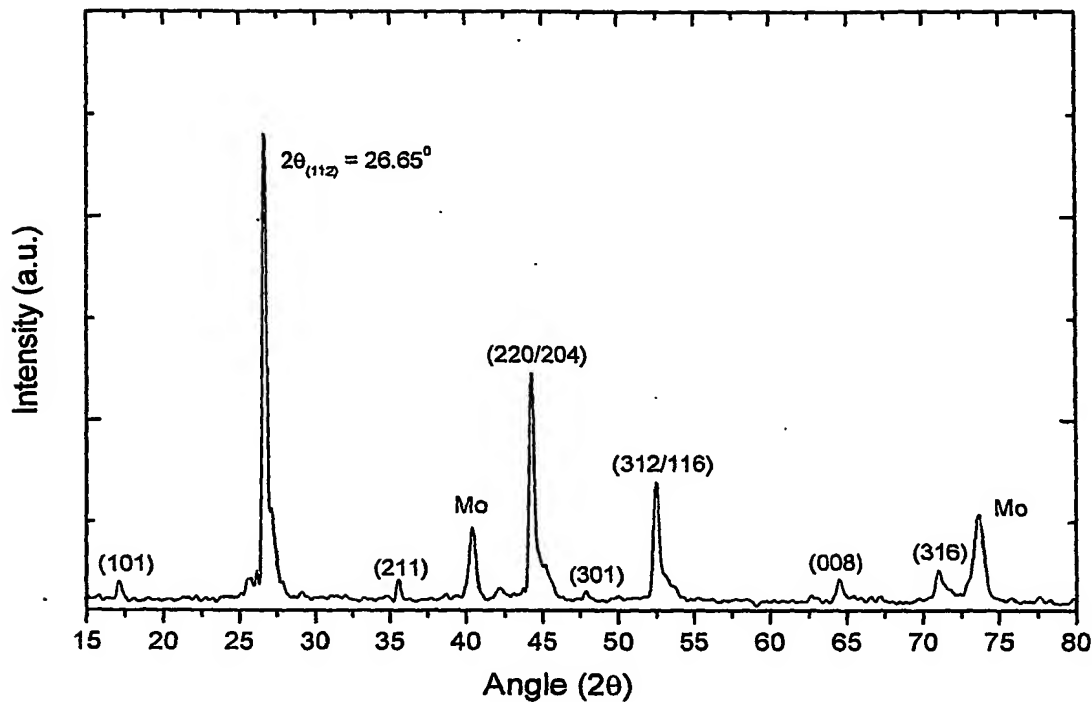


Figure 5.2

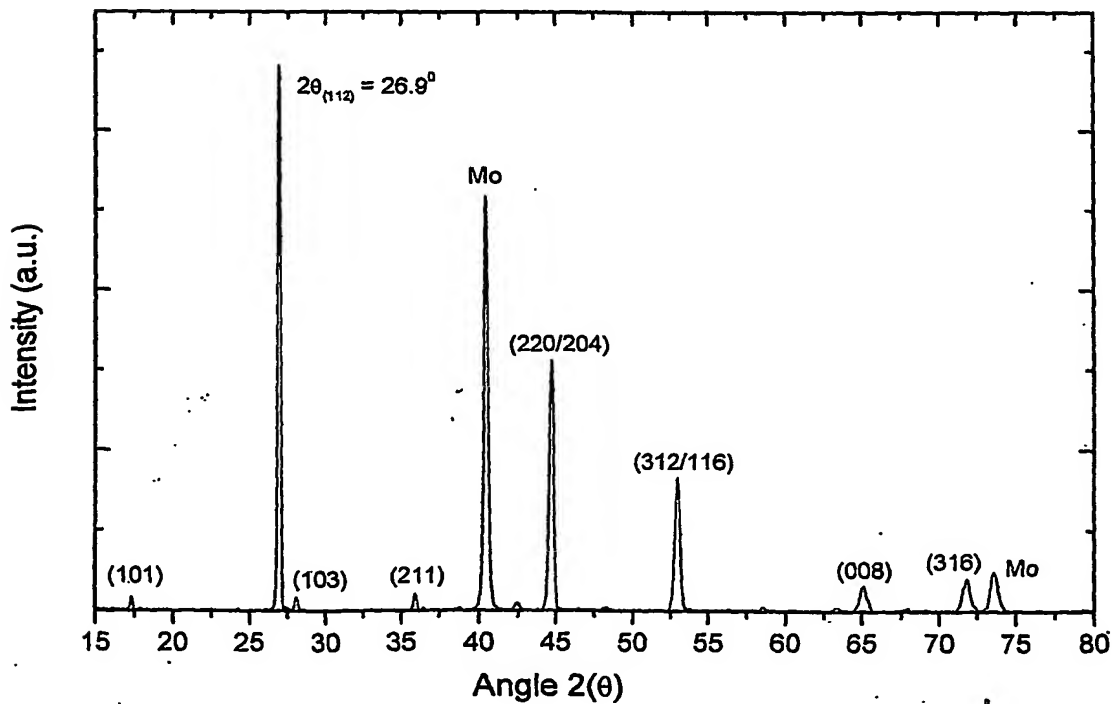


Figure 6.

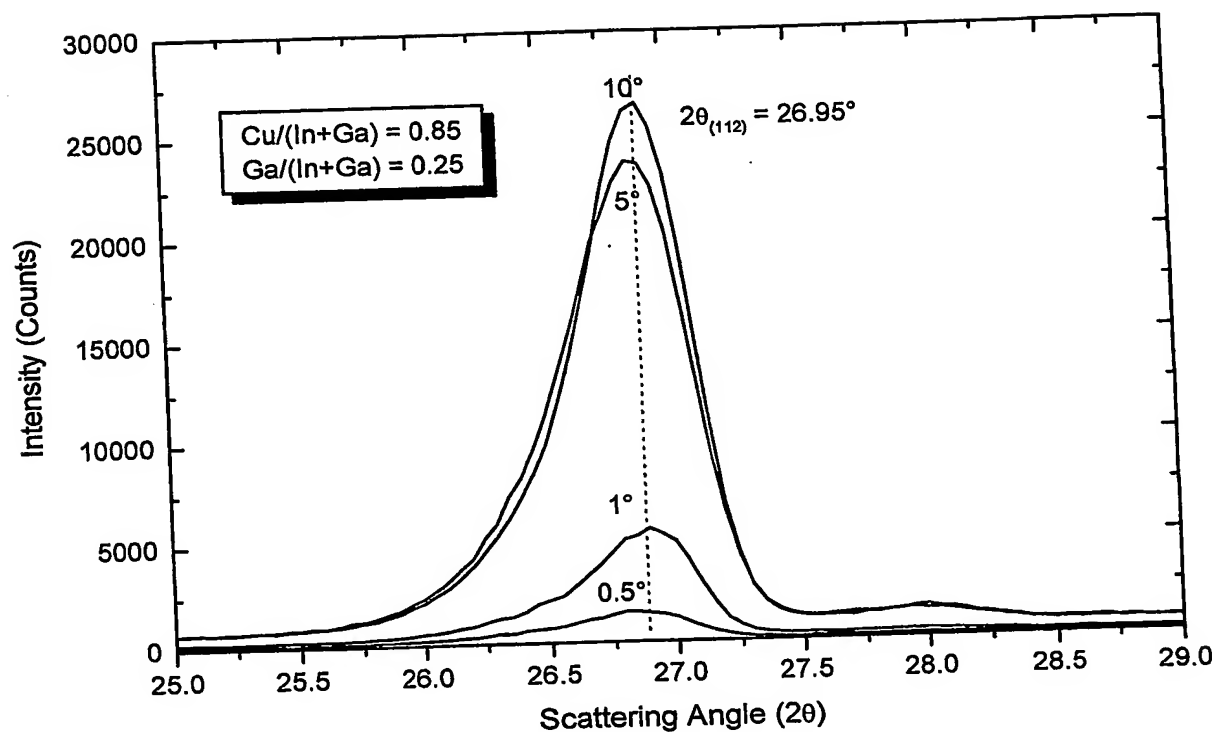


Figure 7.1.

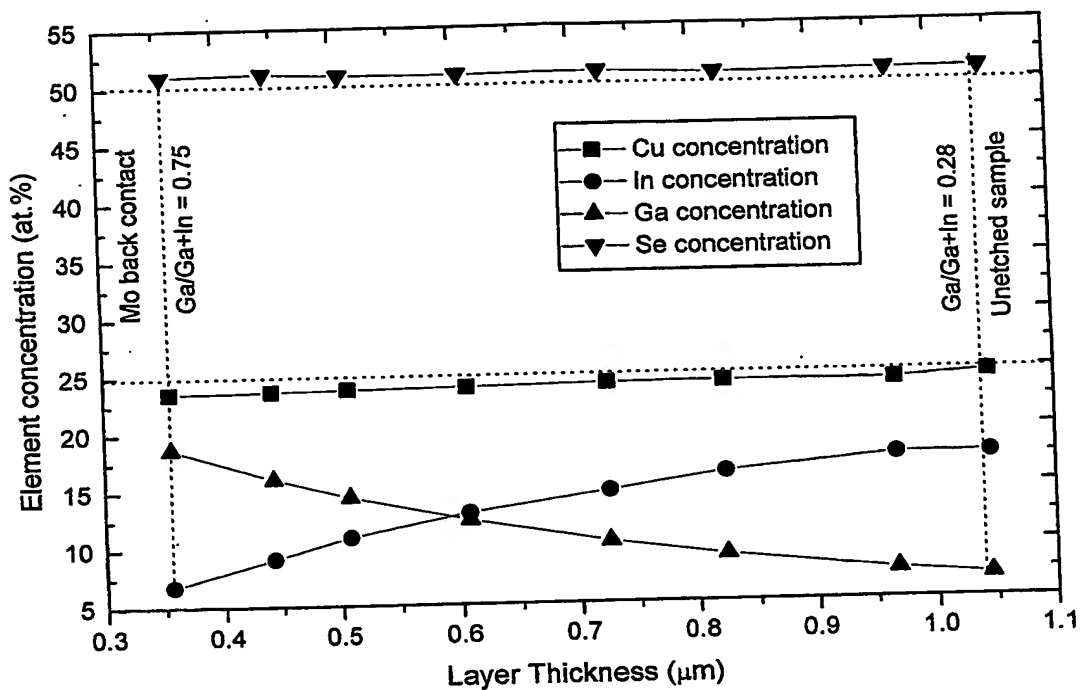


Figure 7.2.

